

(telethermal) environment, and the prospect of encountering more fluorite at deeper levels is negated.

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SPECTROPHOTOMETRIC DETERMINATION OF MICRO QUANTITIES OF GOLD WITH CETYLTRIMETHYLAMMONIUM BROMIDE IN PRESENCE OF IODIDE

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THE reagents $[\text{Fe}(\text{phenanthroline})_3^{2+}]^1$, tetraphenylarsonium chloride², diethyl ether³, Rhodamine B⁴, mesityl oxide^{5,6} or primaquine phosphate⁷ have been used in spectrophotometric methods for determination of gold. In the present investigation

we noted that gold(III) forms an yellow ion-association complex with cetyltrimethylammonium bromide (CTAB) in presence of potassium iodide and is extractable into chloroform. Based on this a simple spectrophotometric method for the determination of gold is reported.

A stock solution of Au(III) was prepared by dissolving gold chloride (Johnson and Matthey) in distilled water and standardizing⁸. Solution of lower concentration of the metal was prepared by appropriate dilution of the stock. Aqueous solutions of CTAB (0.025 M SISCO) and potassium iodide (0.03 M BDH) were used. KH_2PO_4 -NaOH buffer was employed to adjust the pH of the aqueous solution. Standard solutions of diverse ions were prepared from their salts. Chloroform and other solvents were distilled before use. All other reagents used were of analytical grade.

Absorbance measurements were made with a Shimadzu PR1 model recording spectrophotometer. Stopped quartz cells of 10 mm optical path length were used for all measurements. An ECL 5651 digital pH meter was used to measure the acidity of the aqueous solution.

To an aliquot containing Au(III) (70 μg) were added potassium iodide (1 ml) and CTAB (0.1 ml). The mixture was adjusted to pH 7.0 with buffer. The volume of the aqueous phase was made up to 10 ml. The mixture was then equilibrated (30 sec) with chloroform (10 ml). The separated organic layer was dried over anhydrous sodium sulphate. Finally the absorbance of the chloroform extract was measured at 290 or 360 nm against a blank prepared in a similar manner. The amount of gold was computed from a calibration curve. To test for interference by other ions, the ions were added to the system before addition of the reagents.

When potassium iodide was added to a neutral or slightly acidic solution containing gold(III), a yellow coloration due to the formation of $[\text{AuI}_4]^-$ was formed. This complex anion was not extractable into chloroform. On addition of an aqueous solution of CTAB to the coloured solution, an ion-association complex, probably of the type $[\text{CTA}]^+ [\text{AuI}_4]^-$, was formed. This was extractable into chloroform. Other solvents like ethyl acetate, benzene and 1,2-dichloroethane were also tested as extracting solvents, but these offered no special advantages over chloroform (table 1). The complex was not extractable into carbon tetrachloride.

The reagent blank itself shows absorption maximum at 250 nm and the absorption becomes

Table 1 Absorption maxima and molar absorptivities of Au(III)-I-CTAB complex extracted into different solvents

Solvent	Absorption maxima (nm)	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$) ($\times 10^{-4}$)	Sensitivity ($\mu g/cm^2$)
Chloroform	290	2.14	0.009
	360	1.29	0.015
Benzene	298	1.97	0.010
	365	1.32	0.014
Ethyl acetate	290	2.08	0.009
	360	1.13	0.017
1,2-Dichloroethane	295	1.77	0.011
	365	1.07	0.018
Carbon tetrachloride*	—	—	—

*Complex not extractable.

insignificant beyond 290 nm. Hence all absorption measurements were made at 290 or 360 nm. The Au(III) complex showed constant and maximum absorbance when the extractions were carried out in the pH range 0-9, yielding quantitative recovery of gold in a single extraction.

The absorbance of the Au(III)-I-CTAB complex in chloroform showed a linear response up to 15 ppm of gold at 290 or 360 nm. The molar absorptivity of the complex on the basis of gold content worked out to be 2.14×10^4 and $1.29 \times 10^4\ l\ mol^{-1}\ cm^{-1}$, corresponding to Sandell's sensitivities 0.009 and $0.015\ \mu g/cm^2$, at 290 and 360 nm respectively. This classifies the colour reaction (stable for 24 h) as one of the most sensitive for gold. Further, with variation of reagent concentration, it was noted that 1 ml of 0.03 M of KI with 0.1 ml of 0.025 M of CTAB was sufficient to extract 70 μg of gold(III) in a single extraction. Increasing the concentration of the reagent did not bring about any significant change in the maximum value of absorbance.

The average of six determinations of 70 μg of Au(III) was 69.5 μg , with a relative mean deviation of 2.87%. The process is very simple and rapid, requiring only 10-15 min for each run.

In interference tests, an ion was considered to interfere if the recovery of gold differed by more than $\pm 3\%$ from the actual amount. In the present method, gold(III) (70 μg) could be determined without interference in presence of 100-fold excess of Cr(III), V(V), Mo(VI), Hg(II), Rh(III), Al(III), Cu(II), Ni(II), Mg(II), Pt(IV), Pd(II), Zn(II), Cd(II), Pb(II), Zr(IV), Ca(II), Ba(II), Sr(II), Th(IV) and La(III). Fifty-fold excess of Fe(III), Co(II), Mn(II),

Table 2 Analysis of synthetic mixtures

Composition with amounts taken in μg	Recovery of gold (%)
Au(III) 70, Ag(I) 100, Cu(II) 100, Zn(II) 100	98
Au(III) 70, Fe(III) 100, Co(II) 100, Ni(II) 100	98
Au(III) 70, Pd(II) 100, Pt(IV) 100, Rh(III) 100	101

Ag(I) and Bi(III) could be tolerated. U(VI) interfered. Among the anions tested, 200-fold excess of borate, phosphate, tartrate, citrate, fluoride, bromide, phthalate, oxalate, acetate and nitrite, and lower concentrations of ascorbate and EDTA did not interfere in the estimation of gold. Thiocyanate, thiosulphate, thiourea and arsenate interfered.

In the absence of real samples, the applicability of the method was tested by analysing some synthetic mixtures containing Au(III), Ag(I), Cu(II), Zn(II), Fe(III), Co(II), Ni(II), Pd(II), Pt(IV) and Rh(III). The compositions of the mixtures and percentage recovery of gold are given in table 2. The results show that recovery of gold was highly satisfactory. Average of three determinations was taken in each case.

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**PHOTO-SENSITIZED OXIDATION OF
6, 7, 8, 9, 10, 10-HEXACHLORO-1, 5, 5a, 6, 9, 9a-
HEXAHYDRO-6, 9-METHANO-2, 4, 3-
BENZODIOXATHIEPIN-3-OXIDE
(ENDOSULFAN) BY SINGLET OXYGEN**

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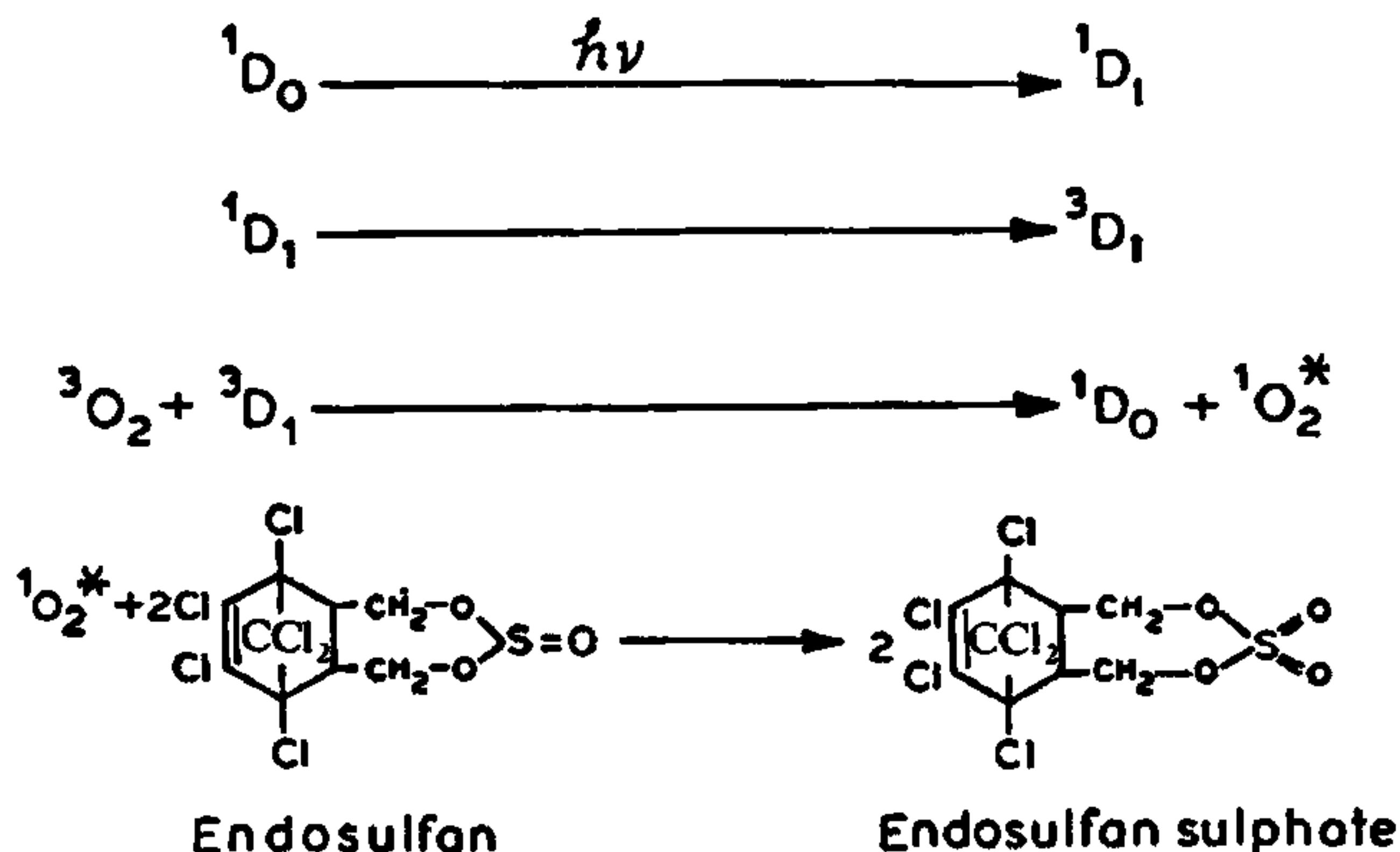
GUNTHER¹ observed that DDT lost its toxic effects quickly when sprayed in the field during summer.

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It was further studied by various workers²⁻⁵. Photodecomposition of aldrin and dieldrin was reported by Henderson and Crosby⁶, whereas Benson *et al.*⁷ characterized the photoproducts of chlordane. Photodecomposition of the chlorinated hydrocarbon endosulfan was observed by Archer *et al.*^{8,9}, while Dureja and Mukerjee¹⁰ did not observe any photosensitization product.

Endosulfan (technical grade) (6, 7, 8, 9, 10, 10-hexachloro-1, 5, 5a, 6, 9, 9a-hexahydro-6, 9-methano-2, 4, 3-benzodioxathiepin-3-oxide), 1, 4-diazobicyclo-(2, 2, 2)-octane (DABCO), methylene blue (CI-52015) and methanol (BDH) were used. All other chemicals used were of SM grade. Endosulfan was used after recrystallization (m.p. 95°C). A 200 W tungsten lamp was used for irradiating the reaction mixture; IR radiations were cut off using a water filter. The reaction mixture was prepared by adding four drops of methylene blue (2×10^{-6} M) in methanolic solution of endosulfan (8% v/v) and was aerated for 5 h in the presence of light. The progress of the reaction was followed by TLC. Some suspension was observed in the reaction mixture after 3 h.

A white substance that settled in the reaction mixture after 5 h was separated by decantation. The methylene blue was removed by the addition of activated charcoal. Dureja and Mukerjee¹⁰ did not observe any photoproduct in methanolic solution with methylene blue in the presence of light from a tungsten lamp while we have obtained a photoproduct, which has been characterized as the sulphate derivative (recrystallized, m.p. 178°C). The following were the results of elemental analysis: found



Scheme 1